Experiment 8.
Galvanic Cells, the Nernst Equation

Experimental Procedure

- Objectives
- Introduction
- Experimental Procedure

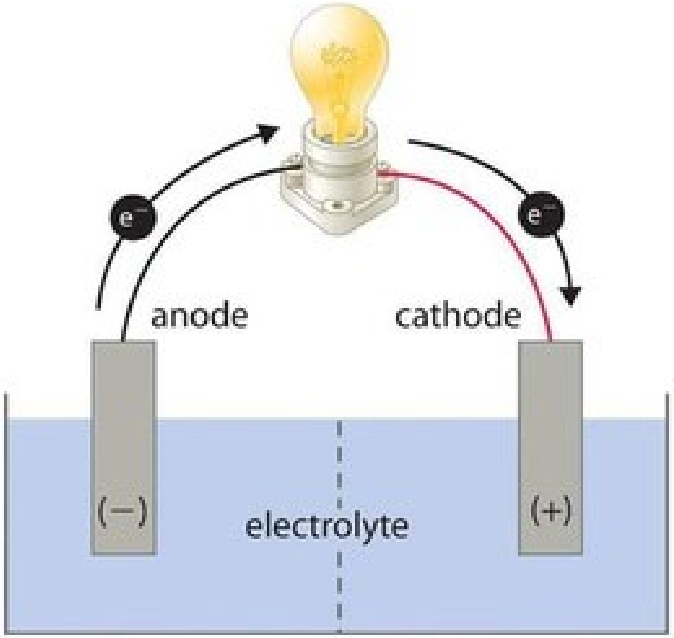
OBJECTIVES

- To measure the relative reduction potentials for a number of redox couples
- To develop an understanding of the movement of electrons, anions, and cations in a galvanic cell
- To study factors affecting cell potentials
- To estimate the concentration of ions in solution using the Nernst equations

INTRODUCTION

An electrolytic cell is an electrochemical cell that drives a non-spontaneous redox reaction through the application of electrical energy. They are often used to decompose chemical compounds, in a process called electrolysis—the Greek word lysis means *to break up*.

A galvanic cell, or voltaic cell, named after Luigi Galvani, or Alessandro Volta respectively, is an electrochemical cell that derives electrical energy from spontaneous redox reactions taking place within the cell. It generally consists of two different metals connected by a salt bridge, or individual half-cells separated by a porous membrane. Volta was the inventor of the voltaic pile, the first electrical battery. In common usage, the word "battery" has come to include a single galvanic cell, but a battery properly consists of multiple cells.



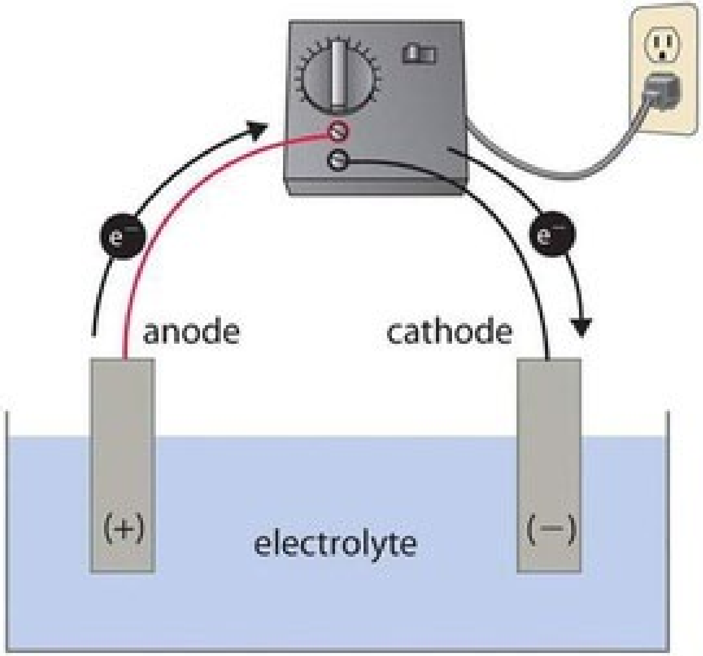
GALVANIC CELL

Energy released by spontaneous redox reaction is converted to electrical energy.

Oxidation half-reaction:
$Y \rightarrow Y^+ + e^-$

Reduction half-reaction:
$Z + e^- \rightarrow Z^-$

Overall cell reaction:
$Y + Z \rightarrow Y^+ + Z^-$ $(G < 0)$



ELECTROLYTIC CELL

Electrical energy is used to drive nonspontaneous redox reaction.

Oxidation half-reaction:
$Z^- \rightarrow Z + e^-$

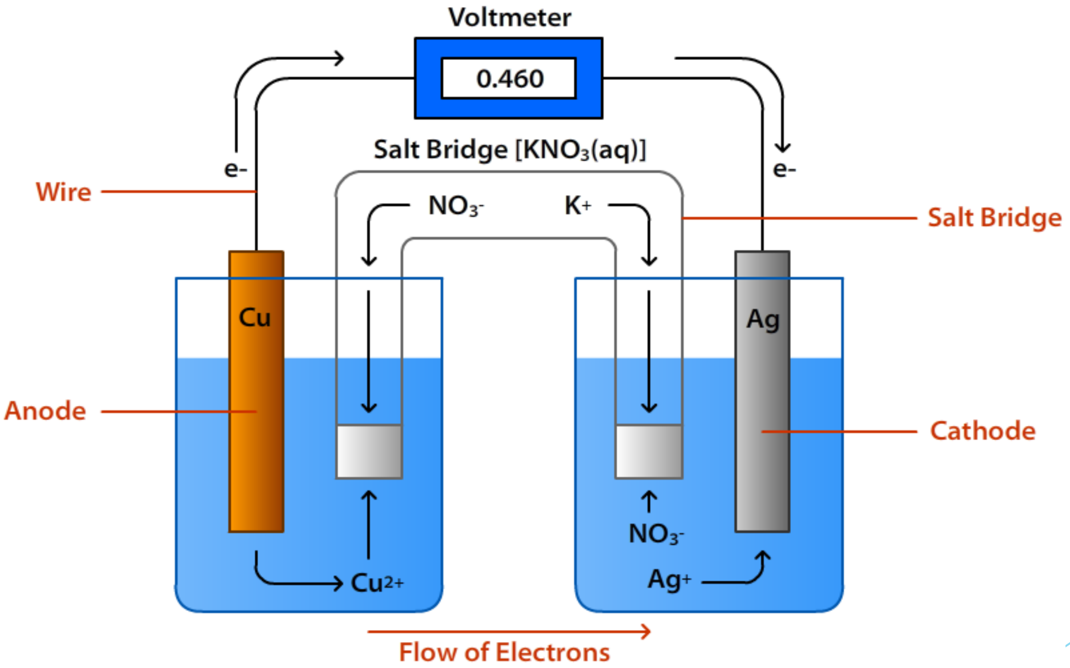
Reduction half-reaction:
$Y^+ + e^- \rightarrow Y$

Overall cell reaction:
$Y^+ + Z^- \rightarrow Y + Z$ $(G > 0)$

$$Cu(s) + 2\,Ag^{+}(aq) \longrightarrow 2\,Ag(s) + Cu^{2+}(aq)$$

$Cu(s) \longrightarrow Cu^{2+}(aq) + 2\,e^{-}$ oxidation half-reaction (redox couple)

$2\,Ag^{+}(aq) + e^{-} \longrightarrow 2\,Ag(s)$ reduction half-reaction (redox couple)



Graphic by Shamsher Singh

Schematic diagram of a galvanic cell

For the copper and silver redox couples, we can represent their reduction potentials as $E_{\mathrm{Cu}^{2+},\mathrm{Cu}}$ and $E_{\mathrm{Ag}^{2+},\mathrm{Ag}}$, respectively. The measured cell potential corresponds to the standard cell potential when the concentrations of all ions are 1 mol/L and the temperature of the solutions is 25°C.

$$E_{\mathrm{cell}} = E_{\mathrm{Ag}^{+},\, \mathrm{Ag}} - E_{\mathrm{Cu}^{2+},\mathrm{Cu}}$$

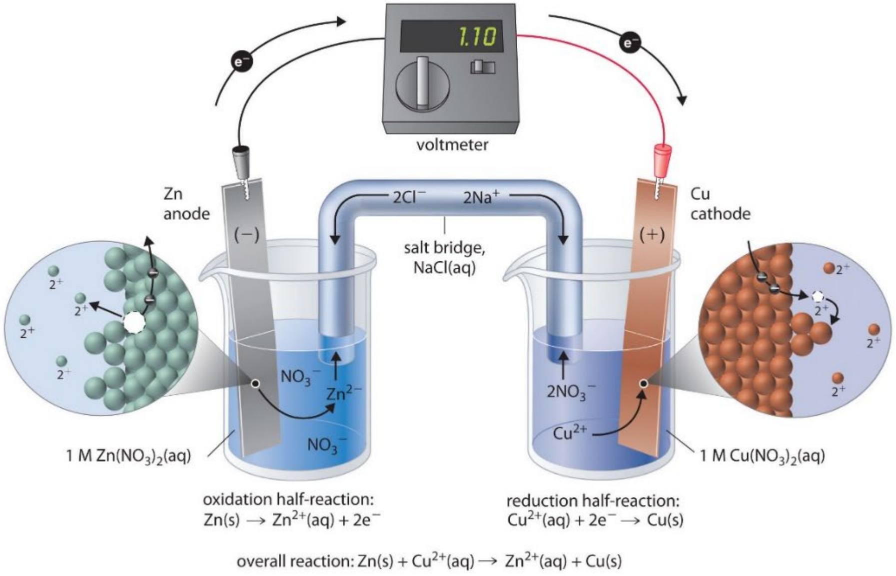
$$E^{o}_{\mathrm{cell}} = E^{o}_{\mathrm{Ag}^{+},\, \mathrm{Ag}} - E^{o}_{\mathrm{Cu}^{2+},\mathrm{Cu}} =$$

$$+0.80\mathrm{V}-(+0.34\mathrm{V}) =+0.46\mathrm{V}$$

Nernst equation

$$\mathrm{Zn}(s) + \mathrm{Cu}^{2+}(aq) \longrightarrow \mathrm{Cu}(s) + \mathrm{Zn}^{2+}(aq)$$

$$E = E^0 - \frac{0.0591}{2}\log(Q)$$ $Q = [Zn^{2+}] / [Cu^{2+}]$



(a)

(b)

$$E = E^0 - \frac{0.0591}{2}\log(Q)$$

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Cu(s) + Zn^{2+}(aq)$$

$$E_{cell} = E^{o}_{cell} - \frac{0.0592}{2} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

Rearrangement of this equation (where E^{o}_{cell} and $[Zn^{2+}]$ are constants in the experiment yields an equation for a straight line:

$$E_{cell} = E^{o}_{cell} - \frac{0.0592}{2} \log [Zn^{2+}] + \frac{0.0592}{2} \log [Cu^{2+}]$$

$$y \quad = \quad b \quad + \quad m \quad x$$

$$E_{cell} = constant - \frac{0.0592}{2} \text{ p Cu}$$

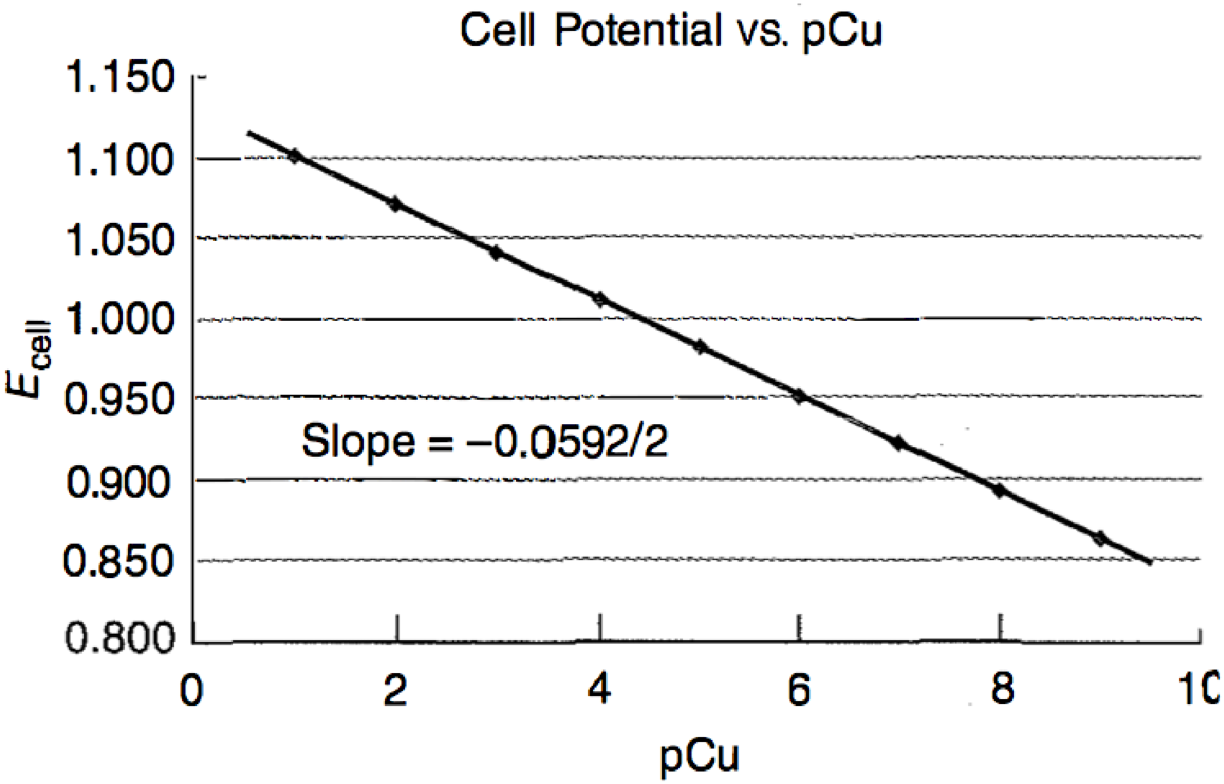


Figure 32.2 The variation of E_{cell} versus the pCu

EXPERIMENTAL PROCEDURE

Overview

The cell potentials for a number of galvanic cells are measured and the redox couples are placed in order of decreasing reduction potentials. The effects of changes in ion concentrations on cell potentials are observed and analyzed.

Part A. Reduction Potentials of Several Redox Couples

1. Collect the electrodes, solutions, and equipment.

1) You will prepare a variety of semi-microscale voltaic cells in a 6-well test plate and fill them three-fourths full of the 0.1 M solutions as shown in Figure 32.3. Share these solutions with other groups of chemists in the laboratory.

2) Polish strips of copper, zinc, magnesium, and iron metal with sand paper, rinse briefly with dilute (~1 M) HNO_3 (Caution!), and rinse with deionized water.

3) The polished metals, used as electrodes, should be bent to extend over tip of their respective beakers. Check out a voltage probe (Figure 32.4) with two electrical wires attached to alligator clips.

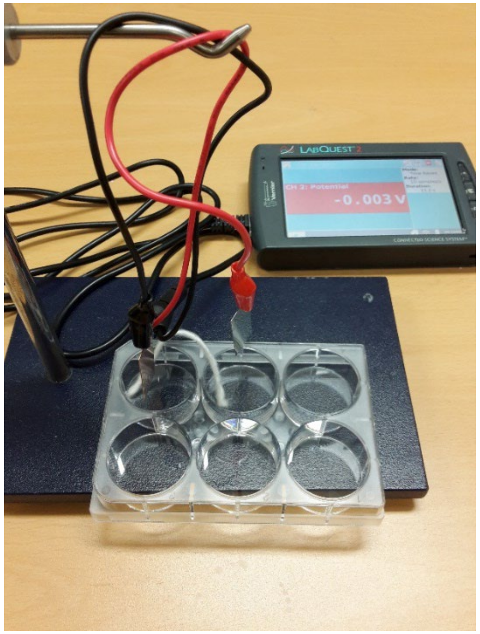


Figure 32.3 Setup for measuring the cell potentials of six galvanic cells

2. Set up the copper–zinc cell.

1) Place a Cu strip (electrode) in the $CuSO_4$ solution and a Zn strip (electrode) in the $Zn(NO_3)_2$ solution.
2) Make a salt bridge by soaking a short length of cotton string in a beaker that contains a small amount of 1 M KNO_3 solution. Connect the Cu and Zn cells with the cotton string.
3) Connect a Voltage Probe the Channel 1 of the Vernier interface.
4) Connect one electrode to the negative terminal of the probe and the other to the positive terminal.

3. Determine the copper–zinc cell potential.

1) If the interface reads a negative potential, reverse the connections to the electrodes. Read and record the (positive) cell potential. Identify the metal strips that serve as the cathode (positive terminal) and the anode.
2) Write an equation for the half–reaction occurring at each electrode. Combine the two half–reactions to write the equation for the cell reaction.[1]

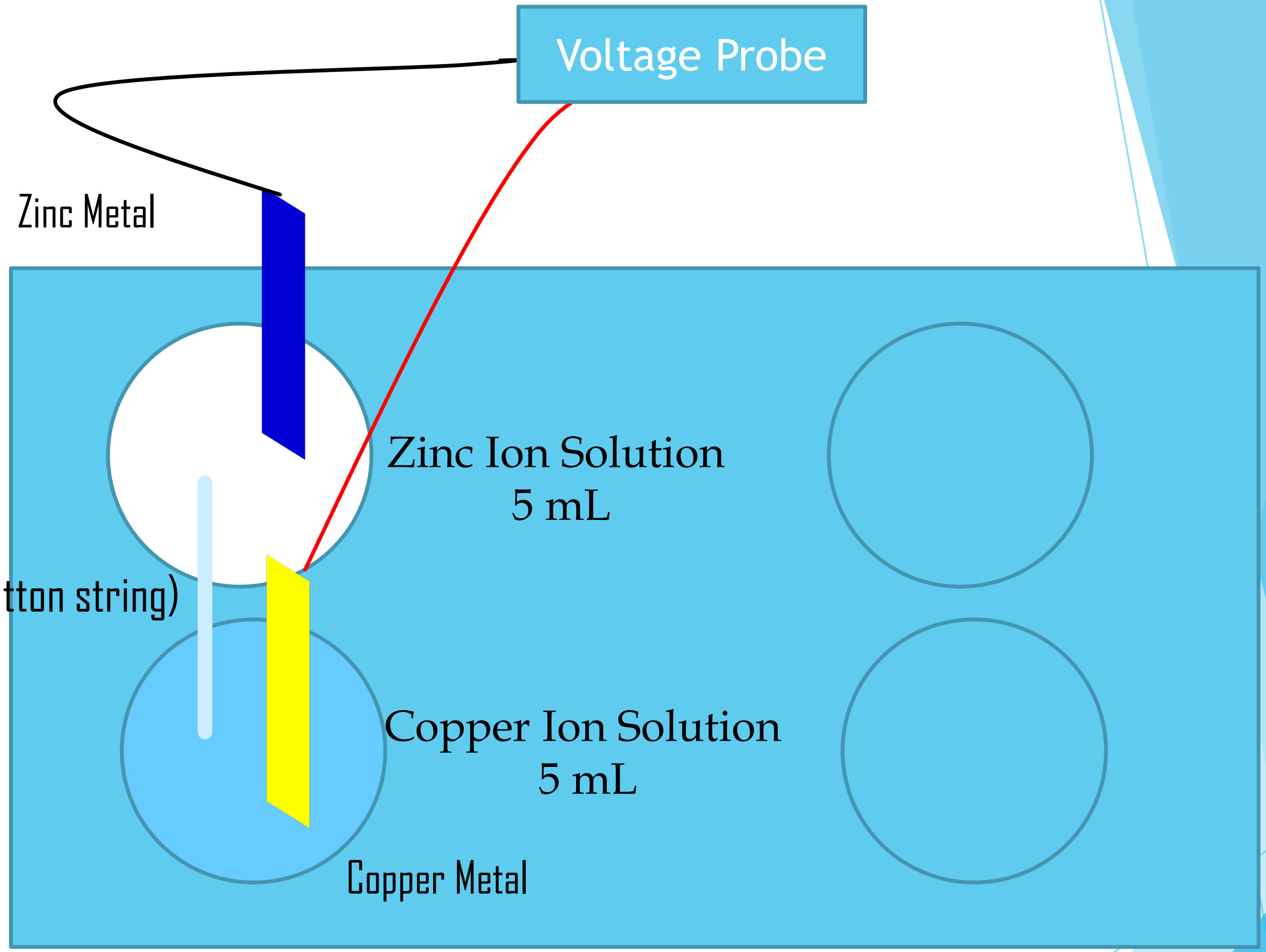
4. Repeat for the remaining cells.

1) Determine the cell potentials for all possible galvanic cells that can be constructed from the four redox couples.

2) Refer to the Report Sheet for the various galvanic cells. Prepare a new salt bridge for each galvanic cell.[2]

5. Determine the relative reduction potentials. Assuming the reduction potential of the Zn^{2+}(0.1 M)/Zn redox couple is −0.79 V, determine the reduction potentials of all other redox couples. [3]

Galvanic Cell	E_{cell} Measured	For the Redox Couple	Reduction Potential (Experimental)	Reduction Potential (Theoretical)
Cu–Zn		Cu^{2+} /Cu		
Zn–Fe		Fe^{2+}/Fe		
Zn–Zn	0	Zn^{2+}/Zn	−0.79 V	−0.79
Zn–Mg		Mg^{2+}/Mg		
Zn–Unknown, X		X^{2+}, X		



Voltage Probe

Zinc Metal

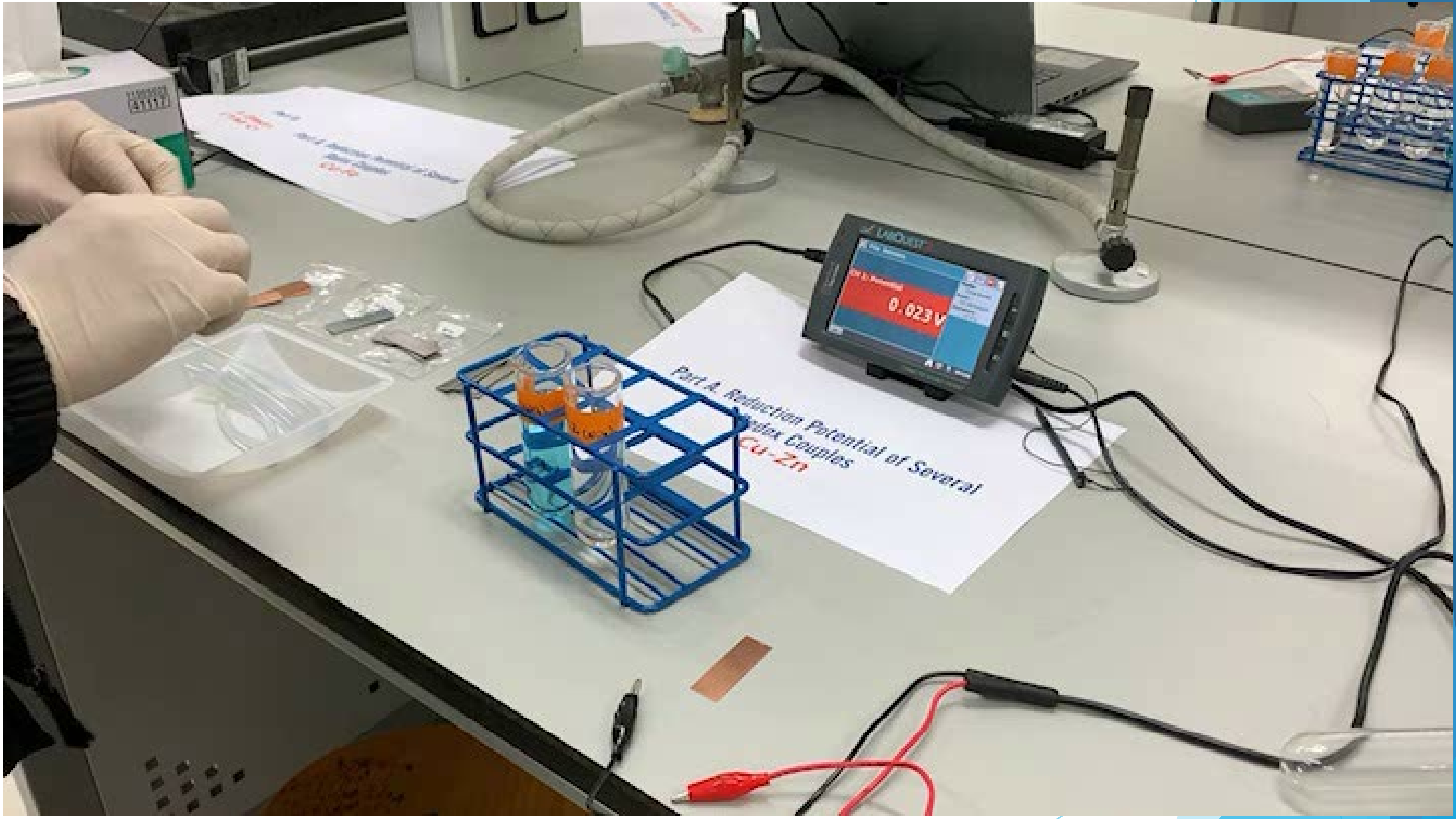
Zinc Ion Solution
5 mL

Salt bridge (Cotton string)

Copper Ion Solution
5 mL

Copper Metal

Copper/Zinc


LabQuest
0.023 V
Part 4. Reduction Potential of Several Redox Couples
Cu-Zn

Galvanic Cell	E_{cell} Measured(V)
Cu–Zn	
Cu–Mg	
Cu–Fe	
Zn–Mg	
Fe–Mg	
Zn–Fe	

Part B. Effect of Concentration Changes on Cell Potential

1. Effect of different molar concentrations.

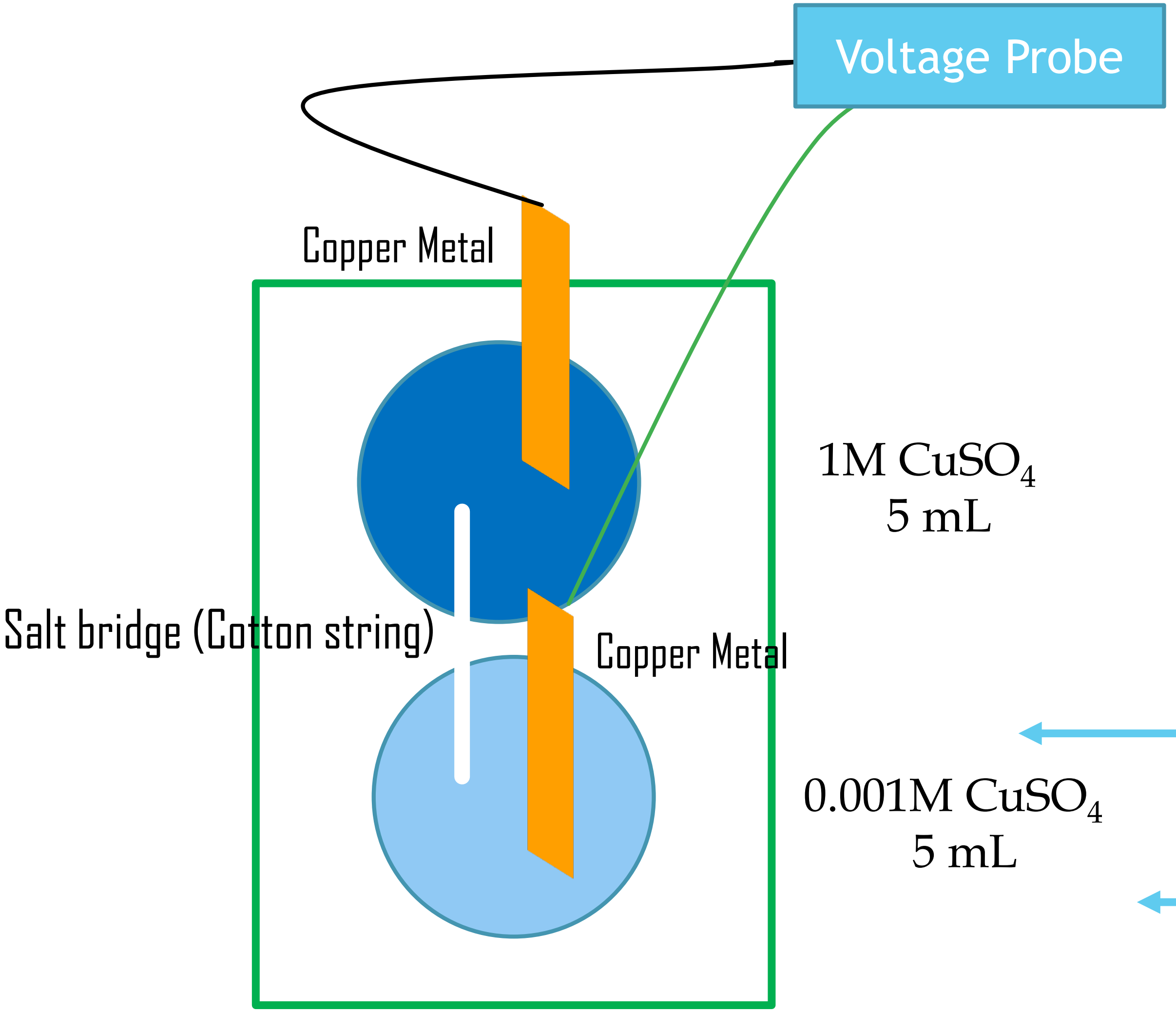
1) Set up the galvanic cell shown in Figure 32.5, using 1 M $CuSO_4$ and 0.001 M $CuSO_4$ solutions. Immerse a polished copper electrode in each solution. Prepare a salt bridge (Part A.2) to connect the two half-cells.
2) Measure the cell potential. Determine the anode and the cathode. Write an equation for the reaction occurring at each electrode.[5]

2. Effect of complex formation.

1) Add 1 mL of 6 M NH_3 to the 0.001 M $CuSO_4$ solution until any precipitate redissolves. (Caution: Do not inhale NH_3.)
2) Observe and record any changes in the half-cell and the cell potential.[6]

3. Effect of precipitate formation.

1) Add 1 mL of 0.2 M Na_2S to the 0.001 M $CuSO_4$ solution now containing the added NH_3. What is observed in the half-cell and what happens to the cell potential? Record your observations.[7]



Voltage Probe

Copper Metal

$1M\ CuSO_4$
5 mL

Salt bridge (Cotton string)

Copper Metal

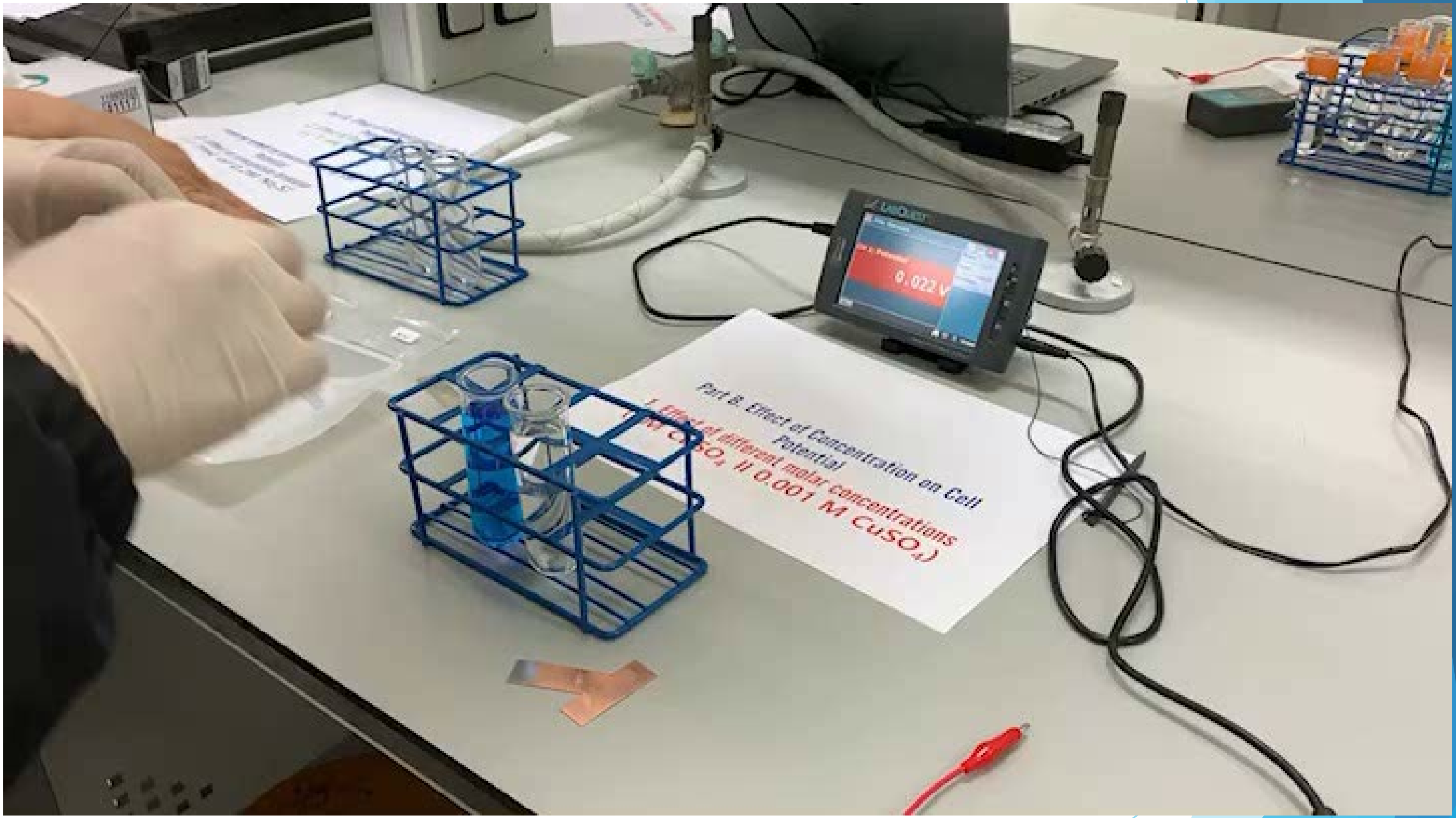
$0.001M\ CuSO_4$
5 mL

1 mL of 6 M NH_3

1 mL of 0.2 M Na_2S

Figure 32.5 Setup for measuring the cell potentials of a Cu^{2+} concentration cell

Effect of Concentration Changes



C. The Nernst Equation and an Unknown Concentration (TA Demonstration)

1. Prepare the diluted solutions.

1) Prepare solutions 1 through 4 as shown in Figure 32.6 using a 1-mL pipet and 100-mL volumetric flasks. Be sure to rinse the pipet with the more concentrated solution before making the transfer. Use deionized water for dilution to the mark in the volumetric flasks.
2) Calculate the molar concentration of the Cu^{2+} ion for each solution and record.[8]

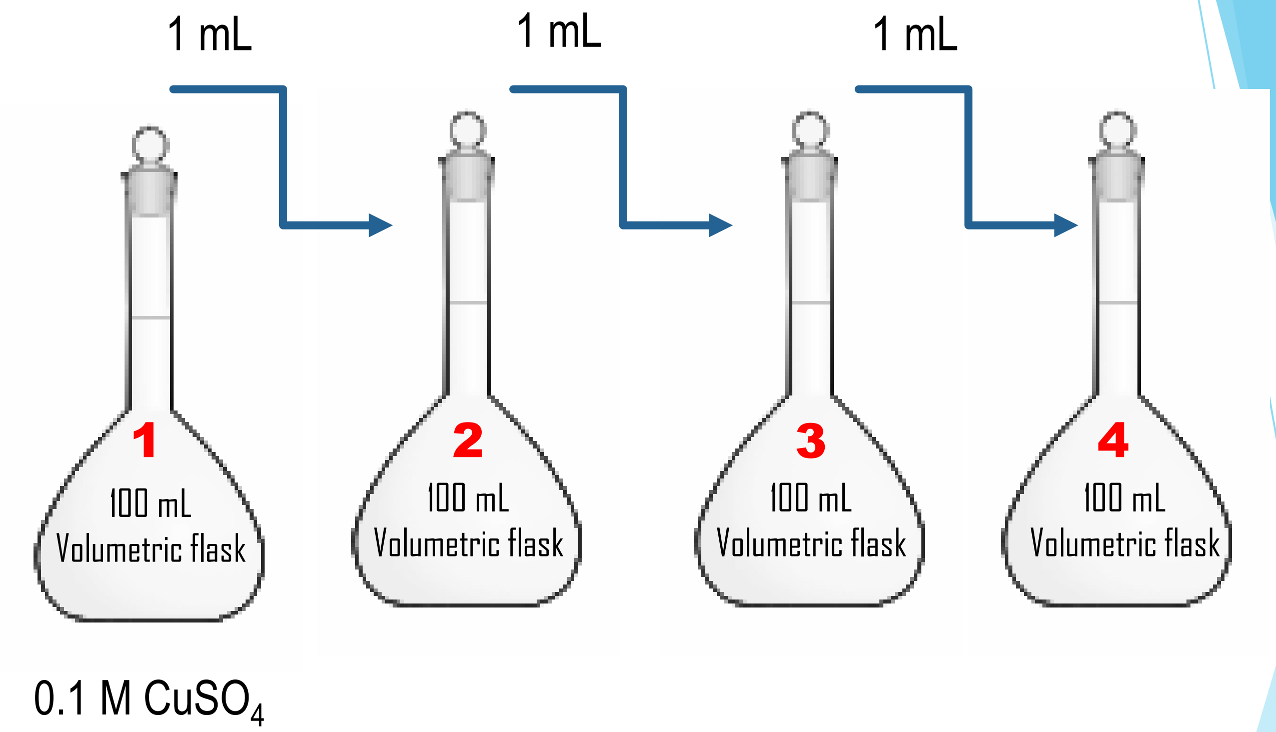


Figure 32.6 Successive quantitative dilution, starting with 0.1 M $CuSO_4$

Solution preparation

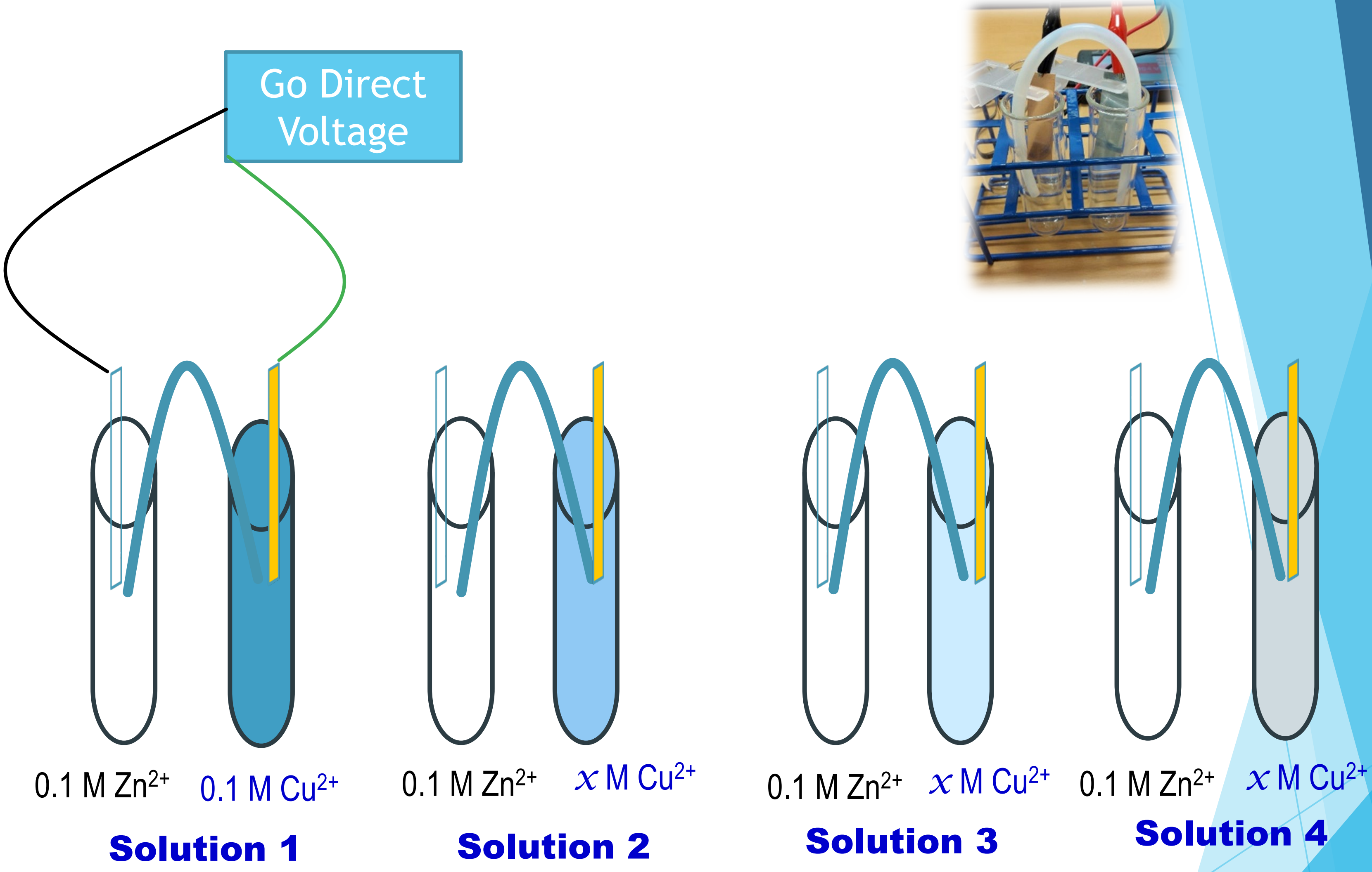
Addition of solution into test tubes

2. Measure and calculate the cell potential for solution 4.

1) Set up the experiment using small (~50 mL) test tube. The Zn^{2+} /Zn redox couple is the reference half-cell for this part of the experiment.
2) Connect the two half-cells with a new commercial salt bridge.
3) Connect the electrodes to the voltage probe and record the potential difference, $E_{cell,expt}$.[9]
4) Calculate the theoretical cell potential $E_{cell,expt}$. (Use a table of standard reduction potentials and the Nernst equation.)[10]

3. Measure and calculate the cell potential for solutions 3 and 2. Repeat Part C.2 with solutions 3 and 2, respectively. A freshly prepared salt bridge is required for each cell.

4. Plot the data. Plot $E_{cell,expt}$ and $E_{cell,calc}$ (ordinate) versus ***pCu*** (abscissa) on the same piece of linear graph paper (page 362) or by using appropriate software for the four concentrations of $CuSO_4$ (see data from Part A.3 for the potential of solution 1). Have your TA approve your graph. [11]



Go Direct Voltage

0.1 M Zn^{2+} 0.1 M Cu^{2+}

Solution 1

0.1 M Zn^{2+} x M Cu^{2+}

Solution 2

0.1 M Zn^{2+} x M Cu^{2+}

Solution 3

0.1 M Zn^{2+} x M Cu^{2+}

Solution 4

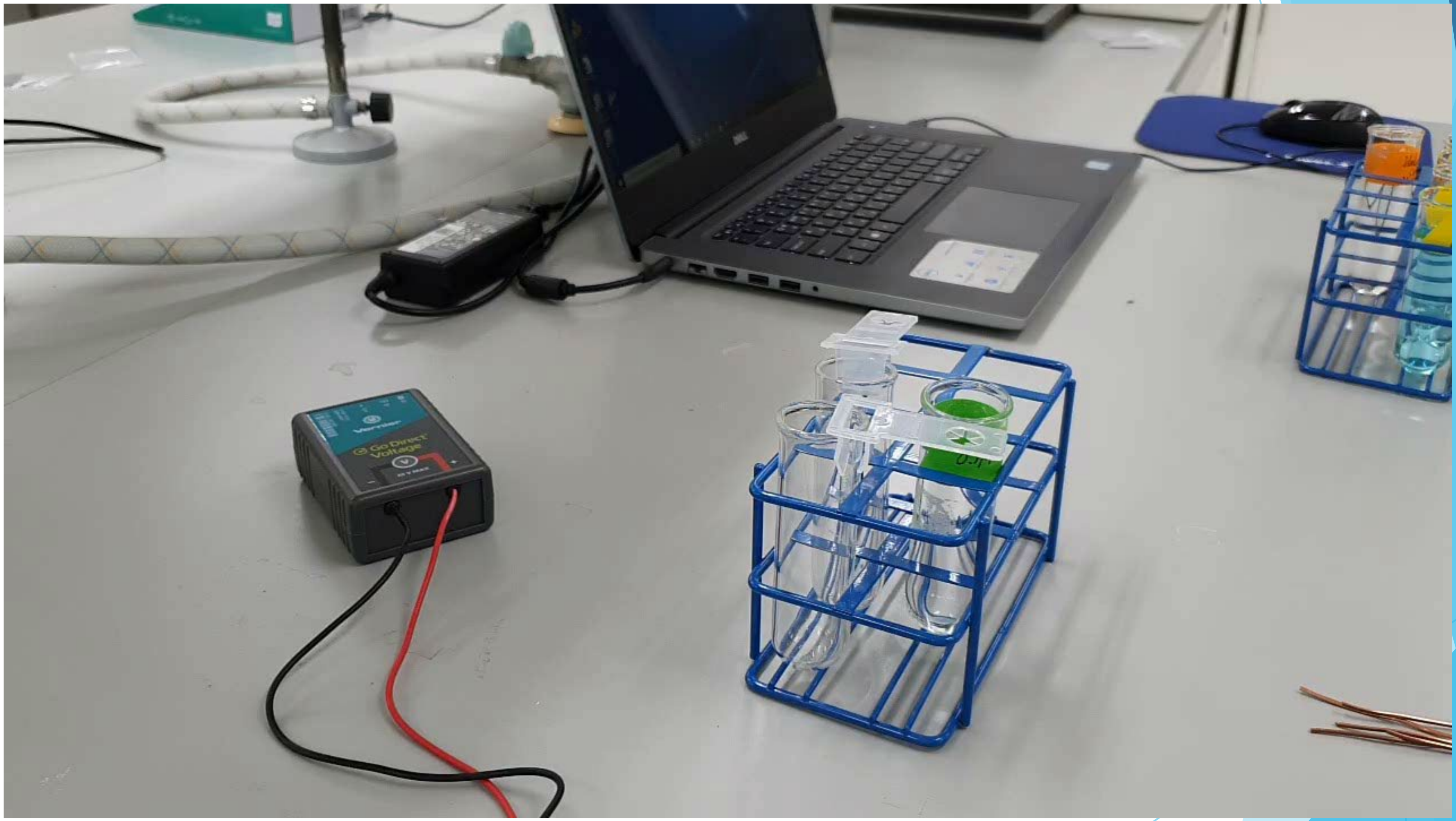
Figure 32.7 Setup to measure the effect that diluted solutions have on cell potentials

5. Determine the concentration of the unknown.

1) Obtain a $CuSO_4$ solution with an unknown copper ion concentration from your TA and set up a like galvanic cell. Determine E_{cell} as in Part C.2.
2) Using the graph, determine the unknown copper(II) ion concentration in the solution.[12]

Cell Potential measurement at Go Direct Voltage probe from Analysis Program in computer

Off-Screen Experimental Video



Solution Number	Concentration of $Cu(NO_3)_2$	E_{cell} (Experimental)	$-\log[Cu^{2+}]$ (pCu)
1	0.1 mol/L		1
2			
3			
4			
5 (unknown concentration)			

Cleanup

Rinse the beakers twice with tap water and twice with deionized water. Discard the rinses in the Waste Metal Solutions container.